TO: Tobi Jones, Assistant Director
Division of Registration and Health Effects

HSM-02027

FROM: Sally Powell, Senior Environmental Research Scientist
Worker Health and Safety Branch
445-4248

DATE: August 28, 2002

SUBJECT: COMMENTS ON DOW AGROSCIENCES MEMORANDUM COMPARING MODELED AND MEASURED 1,3-DICHLOROPROPENE AIR CONCENTRATIONS IN KERN COUNTY (DATA PACKAGE ID# 195675-E)

This is in response to your request for comments on the July 27, 2002 memorandum from Ian van Wesenbeeck and Bruce Houtman of Dow AgroSciences (DAS) to Bryan Stuart and Brian Bret of DAS, "A comparison of modeled and measured 1,3-dichloropropene air concentrations in Kern County, California, 2000 and 2001" (Data Package ID# 195675-E). The memorandum compared concentrations modeled by DAS in its ongoing effort to develop township-specific use limits for 1,3-dichloropropene (1,3-d) to concentrations measured by the California Air Resources Board in July and August of 2000 and 2001 (ARB, 2000 and 2002).

The DAS memo reports two comparisons. First, the frequency distribution of 24-hr concentrations measured by ARB in 2000 and 2001 is compared to a probability distribution of 24-hr concentrations produced by the DAS model. The ARB concentrations are all lower than the modeled distribution. Second, estimates of annual average concentration at each ARB site are compared to a probability distribution of annual concentrations from the DAS model. The ARB concentrations fall between approximately the 50th and 99th percentiles of the DAS distribution. DAS concludes that monitored concentrations fall within the range predicted by the model.

My evaluation is that the comparison is not meaningful because the conditions simulated by DAS were too different from conditions during ARB monitoring and because the concentrations compared were not commensurate. Table 1 summarizes and compares the conditions (inputs) and outputs of the DAS model and the ARB monitoring. (Much of this information is not contained in the July 27 DAS memo, but comes from Ian van Wesenbeeck's answers to a list of questions I sent him; the questions and his answers are Attachment 1.)

Table 1. Comparison of parameters of DAS modeling and ARB monitoring.

DAS MODELING	ARB MONITORING
24-hr concentrations simulated for each point on a grid of "receptors" for every day for 20 years	24-hr concentrations measured at each of six "receptors" 4 days/week during July and August for two years.
Receptors spaced evenly over a 3x3-township area	Receptors (ARB monitoring sites) located throughout the 1,3-d use area of Kern County, comprising approximately 55 townships (including 18 without use).
90,250 adjusted lbs of 1,3-d use simulated annually in center township, none in the other 8 townships.	838,545 adjusted lbs of 1,3-d used annually in Kern use area. 4 monitoring sites in townships with 1,3-d use both years, one in one year, one in neither year. 1,3-d used in an average of 5 of the adjacent townships each year (range 3-7).
[a] Annual average daily 1,3-d use affecting each receptor = 28 adjusted lbs/day.	[a] Average daily 1,3-d use in July-August affecting each site = 319 adjusted lbs/day.
Characteristics of the simulated applications (depth, rate, acres treated and day of year) sampled from frequency distributions based on actual use in all of Kern County in 1999-2001 (data from CropData Management Services, Inc.). Application locations assigned randomly within the township.	Actual Kern County applications, July-August, 2000 and 2001.
Hourly weather conditions supplied to simulation from several years of Merced weather data.	Actual Kern County weather conditions, July-August, 2000 and 2001.
Model outputs for comparison to monitoring: 1. Distribution of the annual *maximum* 24-hr concentrations at all receptors (20 annual maxima per receptor) 2. Distribution of annual *average* concentrations at all receptors (20 annual averages per receptor)	Data compared to modeling outputs: 1. Distribution of *all* 24-hr concentrations from July-August at all sites for two years 2. Annual average concentration at each site in 2001 (calculated assuming all concentrations other than July-August were at detection limit)

[a] Calculation explained in Attachment 2.

Comparison of modeled and monitored conditions

Use and weather are principal determinants of fumigant air concentrations. The modeling and monitoring differed enough on both factors that the resulting concentrations are not comparable.

Use

Both the amount and spatial distribution of use influence air concentrations. Precise comparison of modeling and monitoring in these respects is difficult, because it is not possible to identify the geographic areas whose 1,3-d applications determined the concentrations at each monitoring site or modeling receptor. Li *et al*. (2001) showed that 8-week average methyl bromide concentration could be predicted accurately from use in the 7x7-mile area around a monitoring site. For the purpose of estimating annual 1,3-d concentration at each ARB site (Powell, 2002), 8-week average concentration at each site was regressed on 1,3-d use in the township containing the site plus the closest adjacent township. The 2-township area was used because it was not possible, using the available data, to identify a 7x7-mile area centered on the monitoring site. The prediction was not as good as for methyl bromide, but the regression was significant and R^2 was 0.62. If these 2-township areas are considered the relevant use areas for the ARB sites, daily use affecting ARB sites during July and August averaged 298 lbs/day. These are “raw” pounds, i.e., not adjusted by the application factors used to calculate township use caps. Use in the DAS model is in terms of adjusted pounds. The average application factor in Kern County in July and August of 2000 and 2001 was 1.07 (based on use records of Crop Data Management Services, Inc.), making average daily use 319 adjusted lbs/day. When the same 2-township assumption is applied to receptors in the DAS simulation, the average daily use per receptor is 28 adjusted lbs/day. (These calculations are shown in Attachment 2.)

Weather

Although the DAS model used Merced weather data to represent Kern County, this is probably not a source of great discrepancy. The important difference is that while ARB monitoring was conducted only in July and August, the DAS model simulated concentrations for the full year.

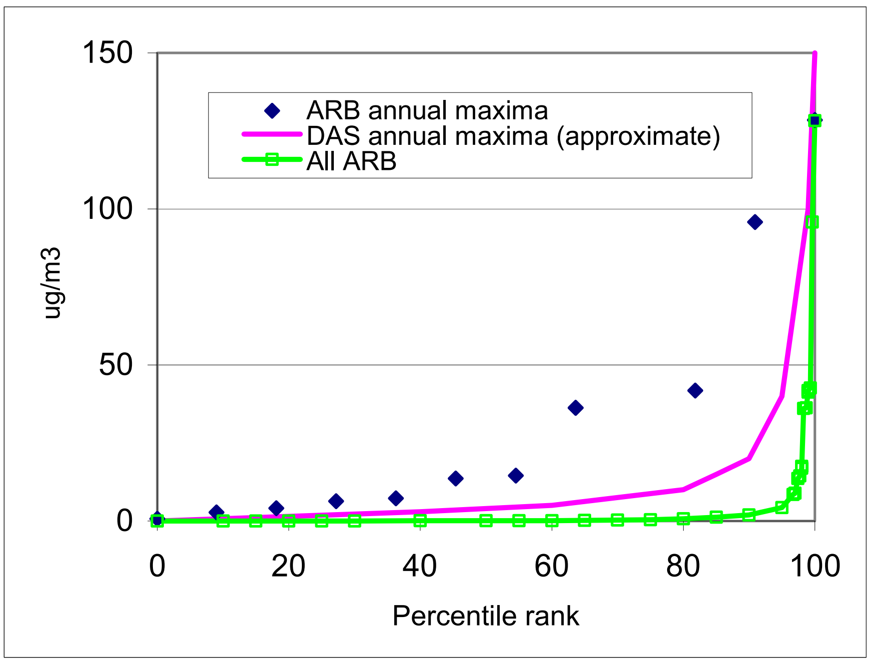
Comparison of modeled and monitored concentrations

24-hour concentrations

From the model output of 20 years of 24-hr concentrations for each receptor, DAS selected the *maximum* 24-hr concentration each year (from all 12 months) for each receptor. The frequency distribution of these annual maxima was compared to the distribution of *all* 24-hr concentrations monitored in July-August of 2001 and of 2000-2001 combined (Figs. 1 and 2 in the DAS memo).

Comparing a distribution of maxima to a full distribution is inappropriate. The full distribution of monitored 24-hr concentrations contains the maxima as its highest values, but the percentile ranks of the maxima are inflated by the inclusion of the lower values. The figure below shows the frequency distributions of 1) the maximum concentration at each ARB site each year, 2) the DAS modeled distribution of yearly maximum concentrations at each receptor, and 3) all ARB monitored 24-hr concentrations. (The DAS distribution was approximated from Fig. 2 of the DAS memo; the actual values were not reported.) The two lower curves are the distributions compared by DAS in their Fig. 2. DAS concluded that only 11 of the ARB 2001 samples (<6%) were above the 50th percentile of the modeled distribution. The individual points are the ARB maxima, which are almost all higher than the corresponding DAS percentiles. The correct comparison suggests that 10 of 12 ARB maxima (83%) are above the modeled 50th percentile.

Fig. 1. 24-hour 1,3-dichloropropene concentrations.



Annual average concentrations

DAS compared annual average concentrations at model receptors to annual averages at the ARB sites. DAS estimated annual averages at ARB sites using the 8-week monitoring-period averages and assuming that concentrations were at the detection limit the rest of the year. They concluded that the monitoring-based annual averages all fell within (between the 50th and 99th percentiles) the modeled distribution.

It is unlikely that concentrations from September through June would be at the detection limit. 1,3-d is used in every month in Kern County. Use in July-August represents only about 27% of the annual total. The peak use period is in the fall, when around 33% of the annual total is applied in a 2-month period. DPR estimated annual average concentrations from the ARB data using pounds of 1,3-d applied in the area in the nonmonitored months and the relationship between use and concentration during monitoring (Powell, 2002). These concentrations are higher than the ones estimated by DAS, all of them falling above the 98th percentile of the modeled distribution (Table 2).

Table 2. Annual average concentrations estimated by DAS and DPR using ARB monitoring data.

Site	Annual average concentration (DAS estimate)[a]	Approximate percentile rank in modeled distribution [a]	Annual average concentration (DPR estimate)[b]	Approximate percentile rank in modeled distribution	Approximate percentile rank in 1994 modeled distribution [c]
ARB	0.07	52	0.69	98	75
MET	0.18	79	1.15	>100	92
MVS	0.21	85	0.72	99	78
SHA	NA	NA	1.14	>100	92
VSD	0.36	93	1.12	>100	92
ARV	0.68	98	1.24	>100	94
CRS [d]	0.07	52	1.08	>100	91

[a] From Table 1 and Fig. 3 of DAS memo.
[b] From Powell (2002); 2 years averaged for sites monitored both years.
[c] Sanborn and Powell (1994).
[d] 2001 only; 2000 value was inexplicably high.

The annual average concentrations estimated by DPR (Table 2) agree more closely with the distribution of long-term average concentrations modeled by DAS in 1994 and used by DPR in the exposure assessment for 1,3-d (Sanborn and Powell, 1994). That distribution included only receptors in the highest-use township of a 9-township use area. In that simulation, average annual use in the 2-township areas affecting receptors was probably between 215 and 295 lbs/day (compared with 28 lbs/day in the latest simulation).

Summary

DAS compared model-simulated distributions of 1,3-d air concentrations to the concentrations monitored by ARB in Kern County and concluded that monitored concentrations fell within the distributions predicted by the model. However, differences between the modeled and monitored conditions, as well as between the concentrations selected for comparison, make the comparison uninterpretable. The amount of use simulated by DAS was far less than actual use during ARB monitoring (28 *vs*.319 lbs/receptor/day). This would produce modeled concentrations much lower than would be expected given actual use in the area. At the same time, DAS selected inappropriately low 24-hr and annual monitoring concentrations for comparison. The appropriate monitoring data show concentrations higher than those modeled, as would be expected due to the greater use. Annual average concentrations estimated from the monitoring data by DPR are more consistent with the concentrations modeled in the 1994 DAS simulation, which simulated use levels much closer to actual 2000-2001 use.

References

ARB. 2000. Ambient air monitoring for methyl bromide and 1,3-dichloropropene in Kern County - Summer 2000. Report dated December 27, Project No. C00-028. Sacramento, CA: Testing Section, Engineering and Certification Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency.

ARB. 2002. Ambient air monitoring for methyl bromide and 1,3-dichloropropene in Kern County - Summer 2001. Final report dated June 18, Project No. P-01-004. Sacramento, CA: Quality Management Branch, Monitoring and Laboratory Division, Air Resources Board, California Environmental Protection Agency.

Li, L., Johnson, B., and Segawa, R. 2001. Empirical relationship between use, area, and ambient air concentration of methyl bromide for subchronic exposure concerns. Appendix C of Methyl Bromide Risk Management Plan for Seasonal Community Exposures, June 2001. Sacramento, CA: Department of Pesticide Regulation, California Environmental Protection Agency. http://www.cdpr.ca.gov/docs/dprdocs/methbrom/rmp0601/rmp-appc.pdf

Powell, S. 2002. Annual average concentrations of 1,3-dichloropropene based on monthly use and air monitoring by the California Air Resources Board: Monterey/Santa Cruz and Kern Counties, 2000 and 2001. HSM-02021. Sacramento, CA: Worker Health and Safety Branch, Department of Pesticide Regulation, California Environmental Protection Agency.

Sanborn, J., and Powell, S. 1994. Human exposure assessment for 1,3-dichloropropene. HS-1634 (revised). Sacramento, CA: Worker Health and Safety Branch, Department of Pesticide Regulation, California Environmental Protection Agency.

Attachments:
1) Supplemental information about modeling obtained from DAS 8-19-02 in response to questions from DPR staff.
2) Calculation of average daily 1,3-d use affecting monitoring sites and model receptors.

cc: Joseph Frank
Bruce Johnson
Numay Reed

ATTACHMENT 1
Supplemental information about modeling obtained from DAS 8-19-02 in response to questions from DPR staff.

The modeling that was presented in the recent memo sent to DPR was conducted prior to the receipt of the ARB monitoring data. The objective of the comparison was not to specifically attempt to validate the DAS model under the exact conditions that were experienced in the ARB monitoring region in 2000 and 2001, or to predict the exact 1,3-D concentrations (in time and space) at the various ARB monitoring sites. The modeling exercise was generated as part of the larger township cap modeling exercise to evaluate the impact of 1,3-D use in DPR's list of 'top ten' townships, of which preliminary results were presented to DPR on May 30, 2002. Kern 28S21E was one of DPR's 'top ten' townships for evaluating the impact of increased township caps. Therefore, the Kern modeling exercise provided a convenient *a priori* dataset of modeled 1,3D concentrations following 'typical' use patterns for Kern County. The modeling was conducted for a 20 year simulation using Merced weather (DPR weather data from Bruce Johnson). Input probability distributions for field size, application rate, timing, and depth were obtained from CDMS data from 1999-2001 for all of Kern County. The simulation was conducted with the center township at a 1X cap (80,250 lbs), and no use in the surrounding townships. The use data from all of the Kern townships was chosen since use in the township of interest (28S21E) was so limited and there was no use in surrounding townships from 1999-2001. Using all the Kern data to develop the input distributions provided a more realistic pattern of use and seemed appropriate considering the 20 year length of the simulation. The simulations generated 24-hour maximum and annual average concentrations at EACH receptor in the 9 township grid for each year of simulation. The 24-hour maximum concentration at each receptor represents the maximum concentration observed at that receptor at any time during a given simulation year. Eight-week average concentration's were not generated, however the model is capable of calculating this if needed.

Were 8 weeks of 24-hr concentrations simulated for township 28S21E and 8 other townships? Which were the other townships?

24-hour and annual average concentrations were simulated for the entire year for each of 20 years. As you indicated below, there was no use for the surrounding townships, so we simulated the center township at the 1X cap, with no use in the surrounding townships.

Were all 9 townships simulated at the use cap?

No (see above).

Was the period simulated the same as the ARB monitoring period, i.e., July and August?

No, the simulation covered 20 entire years of use at the township cap in the center township, with use spread out through the year according to probability distributions developed from CDMS use data for Kern County (1999-2001). Fields were placed randomly within ag capable areas from year to year. I would estimate from the use data that approximately 40-50% of the applications were made in the July-August timeframe (see also question #6 below), and the remainder mostly in the fall and early winter. However, ALL 24-hour values were used in the distributions, regardless of the time of year, since in some cases the maximum 24-h concentration at a given receptor may have occurred outside the July-August time period.

Does the DAS modeled distribution of 24-hr concentrations consist of all the simulated 24-hr values from all 9 of the townships?

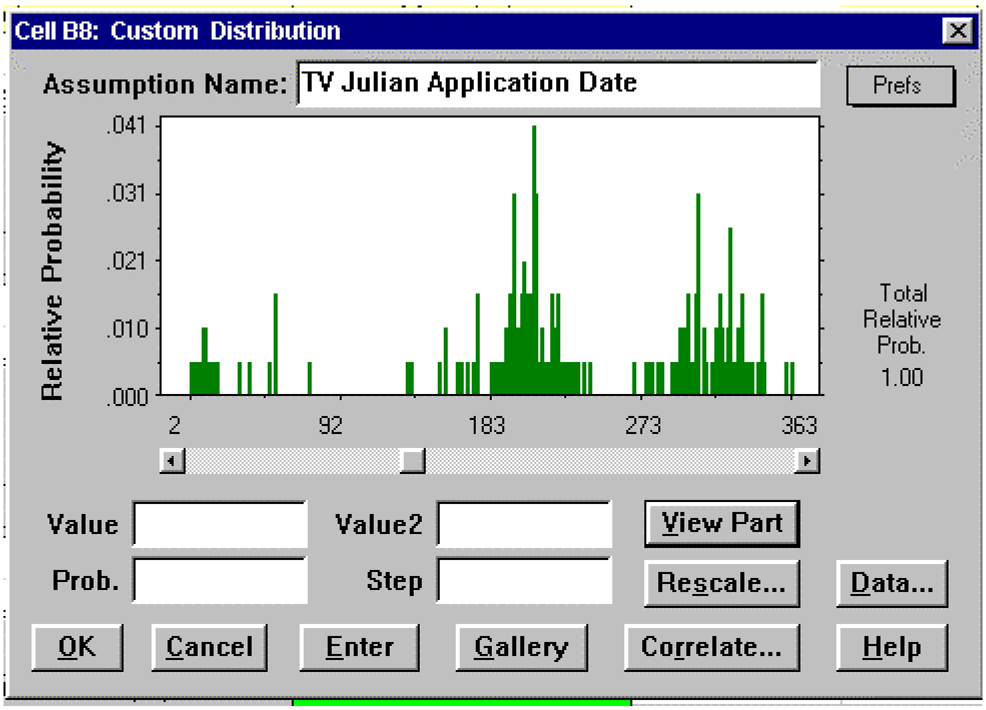
Yes since this represents the potential population that could be exposed to 1,3-D within the modeled township.

What does it mean to model those particular townships for that period, since the weather data were presumably from Fresno and the flux from Salinas, and there was no use of 1,3-d in 28S21E or the 8 adjacent townships in July or August of 1999, 2000 or 2001? I.e., what about the modeling was related to those specific townships and that period?

The purpose of the comparison was to show that the ARB measured values are within the realm of what the model simulates under typical use conditions for Kern County (the modeling was conducted prior to receiving the ARB data). The objective was not to specifically attempt to validate the DAS model under the exact conditions that were experienced in the ARB monitoring region in 2000 and 2001, or to predict the exact 1,3-D concentrations (in time and space) at the various ARB monitoring sites. Clearly this would involve knowing exact site specific weather conditions, and exact field locations, application timings, rates, depths etc. The actual weather file used was Bruce Johnson's Merced dataset. Perhaps if Kern specific weather had been used the results may have varied slightly over the 20 years of simulation however I do not believe that this would have had a major impact on the 20 year 24-h or annual average air concentration distribution. The comparison simply showed that the ARB monitoring results were within the realm of modeled predictions using 20 years of random field placements within a central township.

Can you tell us exactly how much simulated use there was in each modeled township during the July-August period?

This is possible but would be an onerous task to do for each of the 20 years of simulation. Instead, the PDF of application timings that the model selected application dates from is shown below and indicates that approximately 40-50% of the applications may have occurred in the July-August time period.



Is it accurate to say that Fig. 3 in your letter is actually a comparison of 8-week averages, since you calculated annual averages for both ARB and DAS by simply multiplying the 8-week averages by 8/52?

Figure #3 in the memo is a comparison of the annual average concentration distribution for the 20 year simulation and the ARB 2001 data. I extrapolated the ARB data from my calculated 8-week averages to annual averages by assuming weekly 1,3-D concentrations at the LOD (0.05ug/m3) for each of the 44 remaining weeks in the year. I felt that this was reasonably conservative since as shown in Figure #4 in the memo, and by the 20 year modeling, concentrations at a specific receptor location can vary significantly from year to year based on weather, field locations etc.

Differences between my calculated 8-week average concentrations and DPR's calculations are a result of DPR's use of a tolerance interval added to the mean. In order to compare the modeled and measured data, a +/- tolerance limit would need to be applied to the relevant percentiles of the modeled and measured distribution. Presumably adding a tolerance limit on a sub-chronic or chronic exposure estimate based on one season of data can increase the value significantly. Although I have not worked through your calculations/methods in detail, I would imagine that as additional years of data become available and the power of the dataset increases, then the confidence in modeled or measured values at a given percentile should increase and the tolerance limits should decrease? Presumably we would want to use as much data (modeled or measured) as we have available for assessing exposure since season to season and year to year variability at a given location can be significant, as indicated in Figure #4 of the original memo.

2000-2001 ARB monitoring

Use of 1,3-D was determined from the records maintained by Crop Data Management Systems, Inc. (CDMS). Complete use data for 2001 were available from CDMS, but not from DPR's Pesticide Use Reporting system. For consistency, CDMS data were used for both years. Li *et al*. (2001) showed that 8-week average methyl bromide concentration could be predicted accurately from use in the 7x7-mile area around a monitoring site. Because CDMS does not report the section in which an application was made, it was not possible to determine the amount of 1,3-d use in a 7x7-mile square centered on a monitoring site. Instead, use was determined for the township where the site is located plus the adjacent township closest to the section containing the site (Table 2-1). One monitoring site is in a section in the corner of the township; in this case, use in all 3 adjacent townships was considered relevant.

Table 2-1. Townships defining 1,3-dichloropropene use area for each Air Resources Board monitoring site.

		Monitoring site location [a]				
County	**Site**	**Township**	**Section**	**Nearest township(s)**		
Kern	ARB	29S27E	34	30S27E		
	ARV	31S29E	23	31S30E		
	CRS	27S25E	33	28S25E		
	MET [b]	11N20W	1	11N19W	12N20W	12N19W
	MVS	30S29E	30	30S30E		
	SHA	28S25E	10	27S25E		
	VSD	31S29E	19	31S28E		

[a] Corrected locations from Table 1 of Li *et al*. (2001)
[b] Where the monitoring site was in a section at a corner of the township, all 3 adjacent townships were included in the use area.

It was assumed that the applications affecting air concentrations during monitoring were any made 7 or fewer days before the first monitoring date (1,3-D continues to off-gas from soil for 7-14 days after application) and up to but not including the last day of monitoring (little 1,3-D is emitted from soil on the day of application). The dates are shown in Table 2-2.

Table 2-2. Dates of 1,3-dichloropropene applications assumed to determine monitored air concentrations in Kern County.

	Application period	Monitoring period
2000	July 12 – Aug 30	July 19 – Aug 31
2001	June 23 – Aug 29	June 30 – Aug 30

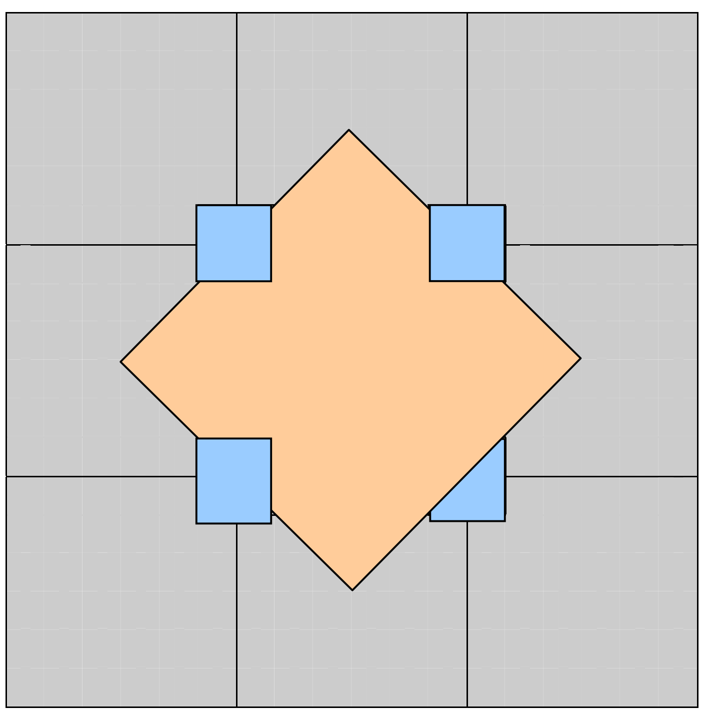
The average number of lbs applied per day in the use area assumed to affect each ARB site is given in Table 2-3.

Table 2-3. Daily 1,3-d use in 2-township areas assumed to affect concentrations at ARB monitoring sites.

Site	Average daily 1,3-D use during monitoring period
2000	-- lbs day $^{-1}$ --
ARB Ambient Air Station (ARB)	0
Cotton Research Station (CRS)	253
Mettler Fire Station (MET)	388
Mountain View School (MVS)	0
Shafter Air Monitoring Stn (SHA)	253
Vineland School District (VSD)	363
2001	
ARB Ambient Air Station (ARB)	0
Arvin High School (ARV)	664
Cotton Research Station (CRS)	292
Mettler Fire Station (MET)	557
Mountain View School (MVS)	126
Vineland School District (VSD)	682
Overall average	**298**

<u>DAS modeling</u>

DAS simulated concentrations at receptors throughout a symmetric 9-township (TS) area, with 90,250 adjusted lbs per year (247 lbs/day) applied in the central TS and none in the other 8 TS. The diagram below represents the 9-TS area.



Applying the same 2-TS algorithm used for the ARB sites (previous section), the peach-colored area in the diagram represents receptor locations affected by the central TS and one TS with no use. They comprise 20% of the total area (64 of 324 total sections) and their average daily use is (0 + 247)/2 = 124 lbs/day. The blue areas represent the corner sections, where receptors are assumed to be affected by use in all 4 surrounding TS. They represent 16 sections or 5% of the total area, and their average daily use is (3*0 + 247)/4 = 62 lbs/day. The gray area (75% of the total) represents receptors whose 2-TS area has no use. The overall average daily use per receptor is therefore (0.2*124) + (0.05*62) = 28 lbs/day.

<u>1994 DAS simulation</u>

In 1994, DAS simulated the distribution of 3-yr average concentrations at receptors in the highest-use ("high-end") township in a 9-TS use area. Average use in the whole 9-TS area was 623 lbs/day (2000 ac/yr x 12 gal/ac x 10.08 lbs/gal x 0.94 ai by wt ÷ 365 days/yr = 623 lbs/day).

Bruce Johnson (personal communication, 2001) has said that use in the high-end TS in the 1994 simulation was close to the current township cap of 90,250 adjusted pounds. If 90,000 lbs were applied in the high-end TS, and the rest evenly distributed among the remaining eight, the average lbs/day used in the high-end TS plus one other would have been (90,000 + 17,176)/365 = 294 lbs/day in a 2-TS area. If only 25% of the total use were in the high-end TS (instead of the 40% comprised by 90,000 lbs), the average use in the two TS would have been 214 lbs/day.